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Monitoring of environmental fingerprints of alcohol ethoxylates in Europe and Canada

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Abstract

Recent improvements in methodology for the determination of alcohol ethoxylates (AE) in effluents now enable measurement of the full range of AE components, at ng/L levels, in the same analysis. This approach was deployed in effluent monitoring of biofilm and activated sludge wastewater treatment plants from Europe ($n = 12$) and Canada ($n = 8$) receiving predominantly municipal effluent. Individual component or "environmental fingerprint" analyses for alkyl carbon numbers C_{12}–C_{18} and ethoxylate numbers 0–18 were conducted using a derivatization procedure with liquid chromatography/mass spectrometry determination. The AE results were very similar with an overall mean level of 5.7 μg/L (range 1.0–22.7 μg/L). The major contribution to the total AE content was from fatty alcohol, which constituted, on average, 43% of the total. The exposure data can then be corrected to account for alcohol derived from sources other than AE and for sorption to particulate matter to determine AE concentrations in undiluted effluents. These data can be used with site-specific dilution information to estimate river water exposure in mixing zones and then to determine aquatic risk by integrating normalized AE effect concentrations determined through quantitative structure–activity relationships.

Keywords: Alcohol ethoxylates; Analysis; Fingerprint distribution; Effluents; Monitoring

1. Introduction

The use of surfactant compounds in industrial and domestic cleaning products results in the potential for "down the drain" discharge of these chemicals. Alcohol ethoxylates (AE) are nonionic surfactants mainly used in laundry cleaning products. The major alkyl chain lengths used are C_{12}, C_{13}, C_{14}, C_{15}, C_{16}, and C_{18} with each chain length ethoxylated with up to 20 ethoxylate (EO) units. Commercial products also contain a small proportion of unethoxylated alcohol. These products are rapidly and extensively degraded in wastewater treatment plants (WWTPs). Previous monitoring studies in Europe and the USA have demonstrated that the average removal of linear AE during activated sludge treatment is >99% (Matthijs, 1996; Fendinger et al., 1995; Gledhill et al., 1989; Matthijs et al., 1999; McAvoy et al., 1998). There were limitations in the analytical methodologies used in these previous studies. To obtain environmental AE concentrations using the HBr scission method (Fendinger et al., 1995; McAvoy et al., 1998) requires an assumption of the ethoxymer distribution. Other studies (Matthijs et al., 1999) employed LC/MS methods which were insensitive to the low EO ethoxymers ($EO_{0–2}$) and looked at only the C_{12}–C_{15} chain length. Consequently, percentage removal values are primarily for C_{12}–C_{15} and $EO_{3–18}$.

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Two mechanisms for degradation of AEs under sewage treatment conditions have been identified: central cleavage leading to polyethylene glycols (PEGs) and the respective alcohol and ω- and β-oxidation of the alkyl chain (Steber and Wierich, 1985). Marcomini et al. (2000) suggest the oxidative central cleavage of linear AEs to be the primary step followed by subsequent degradation of carboxylated PEG.

Battersby et al., (2001) studied the fate of NEODOL 25-7 (a commercial formulation composed of C_{12}–C_{15} homologues with an average ethoxylation of 7 units) and 25-3 (a formulation composed of C_{12}–C_{15} homologues and an average ethoxylation of 3 units) in continuous activated sludge (CAS) units employing influent concentrations in the range 11–13 mg/L. They used a combination of a GC/MS method for the analysis of alcohols and the EO_1 ethoxymer and thermospray LC/MS for $C_{12-18}EO_{2-18}$ to attempt to measure concentrations of AE (as linear $C_{12-18}EO_{0-18}$). However, it was not possible to detect positive residues of the alcohol and the EO_1 ethoxymer, as these components were below the limit of detection for the method ($<2\,\mu g/L$). Increased PEG levels in effluents were consistent with biodegradation of AEs through central cleavage of the hydrophobe and hydrophile to yield the alcohol, which will be rapidly biodegraded by β-oxidation, and PEGs, which are biodegraded more slowly (Holt et al., 1992; van Ginkel, 1996). Despite high removal rates (>97.2%) due to biodegradation, the large volumes of these products used may result in significant environmental discharges; thus effluent fingerprints are needed to facilitate environmental risk assessment. A specific derivatization LC/MS methodology using a reagent (2-fluoro-*N*-methylpyridinium *p*-toluene sulfonate [pyr+]) which permits trace detection (ng/L) by electrospray LC/MS of up to 114 individual species in the range $C_{12-18}EO_{0-18}$ has been developed to fill these needs (Dunphy et al., 2001). The analytical method is validated for linear AE ethoxymers and cannot differentiate between linear and methyl branched AE ethoxymers. In this paper the results of validation of this methodology in another laboratory and application to municipal WWTP effluents from Europe and Canada are described. The resultant homologue-specific distributions (i.e., "environmental fingerprints") from these and other US effluents (Morrall et al., 2005) can be modified by incorporating only that alcohol derived from AE sources (the so-called "alcohol cap"; Wind et al., 2005) and by taking into account any sorption to organic carbon and suspended solids (Van Compernolle et al., 2005) on an ethoxymer-specific basis. The toxicity of individual ethoxymers to aquatic organisms is dependent on chain length and EO number. Recently, a range of new ecotoxicological data (e.g., algal, daphnia, and fish quantitative structure–activity relationships (QSARs), mesocosm studies), as summarized by Belanger et al. (2005), have been generated to expand the database. Exposure and effect findings were integrated in a Toxic Unit (TU)-based model with effects being described as homologue-specific species sensitivity distributions. Acquisition of the detailed environmental concentrations of AEs (i.e., environmental fingerprints) is therefore critical to enable a robust risk assessment from the European, Canadian, and US studies, which conclude low levels of risk for AEs in the aquatic environment for these countries (Belanger et al., 2005).

2. Materials and methods

2.1. Samples

A monitoring survey was initiated by the Environmental Monitoring and Analysis Task Force of ERASM[1] during 2001–2002 to collect and analyze representative samples of effluent from municipal WWTPs in a number of European (EU) countries. Sampling of activated sludge WWTPs was carried out during September–October, 2001 (Netherlands and UK) and during July and December, 2002 (Spain, Italy, and Germany). WWTPs were selected for treatment of predominantly municipal sewage to account for the high tonnage of AE in domestic consumer products. EU effluent samples were collected over a 24-h period in a flow-proportional mode and were preserved by the addition of 8% (v/v) formalin solution at the time of sampling. Details of the WWTPs and the sample collection dates are given in Table 1.

A further monitoring survey (August 2003) was organized with the aim of developing Canadian-specific data on AEs. The Canadian samples were taken from a trickling filter, a rotating biological contactor, and six activated sludge WWTPs. Canadian samples were grab samples, taken around midday, with the specific intention of assuring the highest concentration of AEs possible, so as to avoid issues with detection limits. Consistent with the EU monitoring survey, the Canadian samples were preserved by addition of 8% (v/v) formalin at the time of sampling. A duplicate set of samples from four of these plants, spiked in the field with NEODOL 25-9 (a commercial formulation composed of C_{12}–C_{15} homologues with an average ethoxylation of 9 units) as a check on the integrity of the samples, was also included. Details of the WWTPs and the sample collection dates are given in Table 2.

All effluent samples, typically of 4 L volume, were forwarded to the Shell Global Solutions (UK) laboratory and then stored at 4 °C for a maximum of 1 month until taken for analysis. Previous work (Williams, 2003) has shown that AE when stored with 8% (v/v) formalin over a 3-month period at 4 and 20 °C show no discernable quantitative change when viewed either by carbon chain length or ethoxylate group

[1]ERASM (Environmental Risk Assessment and Management) is a research partnership in Europe of the Association Internationale de la Savonnerie, de al Détergence et les Produits d'Entretien (AISE) and the Comité Européen des Agents de Surface et leurs Intermédiares Organiques (CESIO).

Table 1
Details of the WWTPs used in the ERASM sampling survey

WWTP code	WWTP type[a]	Sample date	Population served	Industrial input (% by volume)	Hydraulic retention time (h)	Influent BOD_5 (mg/L)	Effluent BOD_5 (mg/L)
DM (NL)	AS	21/09/01	40,000	25	12	144	4.3
H (NL)	AS	27/09/01	160,000	20	13	157	4
KV (NL)	AS	25/09/01	300,000	20	7.4–8	112	5
N (UK)	AS	12/10/01	50,000	<10	2–4	350	17.5
C (UK)	AS	15/10/01	71,000	10	11.5–14		
R (UK)	AS	16/10/01	63,500	11	2.6		
E (ES)	AS	20/07/02	140,000	10	11	247	16
V (ES)	AS	20/07/02	320,000	0	9	217	25
M (DE)	AS	28/10/02	750,000	30	19		99% removal
Ra (DE)	AS	11/11/02	65,500	<10	24–30		>98% removal
T (IT)	AS	23/10/02	1,900,000	35	12	140	6
Rb (IT)	AS	12/12/02	195,000	20	14	95	12

[a]AS, activated sludge.

Table 2
Details of the WWTPs used in the Canadian sampling survey

WWTP code	WWTP type[a]	Sample date	Population served	Industrial input (% by volume)	Hydraulic retention time (h)	Influent BOD_5 (mg/L)	Effluent BOD_5 (mg/L)
V (BC)	TF	12/08/03	35,000	10	6		
K (BC)	AS	12/08/03	60,000	10	8–10	250–300	<3
H (O)[b]	AS	07/08/03	750,000	25	—		
LP(Q)[b]	AS	19/08/03	75,000	20	12	160	<10
V (Q)[b]	AS	19/08/03	40,000	10	10	123	<3
P (O)	AS	06/08/03	9000	<10	—	340	<3
C (A)	RBC	11/08/03	3800	<10	—	163	3
W (O)[b]	AS	06/08/03	100,000	30	—	142–236	8–14

[a]TF, trickling filter; AS, activated sludge; RBC, rotating biological contactor.
[b]All these WWTPs were sampled in duplicate and the duplicate spiked with a known quantity of AE standard. These samples were forwarded with the original unspiked effluents to the lab for analysis (See Sections 2.4 and 2.6 for further details of treatment of these samples).

number. This confirmed that AEs were stable under such storage conditions.

2.2. Method summary

A selective and sensitive derivatization LC/MS method based on a method originally developed by Dunphy et al. (2001) was applied to the analysis of individual alcohol ethoxylate homologues in effluent samples from sewage treatment plants. The method used for the analysis of effluents in this paper was essentially as described by Dunphy et al. (2001) but modifications and summaries are included here. Linear alkyl chain lengths of C_{12}–C_{18} and ethoxylate chain lengths from 0 to 18 (where a chain length of 0 indicates the free fatty alcohol) can be measured. C_{17} ethoxylates were not monitored as they are of very limited domestic use. Limits of quantitation (LOQ) for AEs are mostly dependent on the sensitivity of the individual components on the MS detector. The LOQ is the level above which quantitative results may be obtained with a specific degree of confidence (Keith et al., 1983). It is mathematically defined as equal to 10 times the standard deviation of the results for a series of replicates used to determine a justifiable limit of detection. Measured in deionized water, these limits range from 0.2 to 7 ng/L, which equates to a total alcohol ethoxylate content of 0.25 μg/L, based on a 4-L sample size. For effluents these limits may be higher due to coeluting components.

2.3. Materials and equipment

A Finnigan MAT90 magnetic sector mass spectrometer was used for all the analyses. This was used in positive ion electrospray mode with multiple ion monitoring in the range 250–1200 Da. The HPLC column was 15 × 4.6 cm Supelcosil TPR100, heated at 40 °C with a solvent flow of 1 mL/min. Injections were performed automatically with an ISS100 autosampler (Perkin–Elmer) with a 100-μL loop.

C_2 solid-phase extraction (SPE) cartridges (2 g, 12 mL) were manufactured by IST, Hengoed, S. Wales as were the SAX and SCX cartridges (1 g, 6 mL).

The reagent, 2-fluoro-*N*-methyl pyridinium toluene sulfonate (>95%; from Aldrich, Cat. No. 24,955-6) was stored in a desiccator at 4 °C. It was not exposed to the air longer than was necessary. It is a free-flowing cream-colored powder but was discarded when it began to clump together and a fresh supply was used.

All solvents, HPLC, pesticide or AR grade, were obtained from Rathburns, Fisher, or Merck. These included acetonitrile, ethyl acetate, methanol, dichloromethane, formic acid, and triethylamine.

All water used in the method was deionized water from an Elga Maxima Ultrapure system.

Characterized reference standard materials were GENAPOL C100 (contains mainly C_{12} and C_{14} AE, from Clariant Gmbh), GENAPOL T110 (contains mainly C_{16} and C_{18} AE, from Clariant Gmbh), and LUTENSOL AO7 (contains mainly C_{13} and C_{15} AE, from BASF). Data on the ethoxymer composition of each material was available from the suppliers.

The internal standard, deuterated C_{13} alcohol ethoxylate ($C_{13}D_{27}O(CH_2CH_2O)_nH$), was available from Analytical Technology Business Group, Shell Global Solutions (UK), Cheshire Innovation Park, or Shell Chemical Co., Westhollow Technology Center, Houston. During preparation of all standard calibration and sample solutions, 15 μg of the internal standard in 1 mL of acetonitrile was added.

Standards of linear alcohols, dodecanol, tridecanol, tetradecanol, pentadecanol, hexadecanol, and octadecanol, were obtained from Sigma Aldrich at >98% purity. A separate stock solution of each alcohol was prepared in acetonitrile and a 10 μg/mL dilution of the mixed alcohols was used for recovery and calibration fortifications.

2.4. Sample preparation

To achieve sufficiently low LOQs, 4 L of each sample was extracted. The extraction cartridges were thoroughly conditioned before use, to avoid inclusion of compounds from the cartridge that may interfere with the analysis or inhibit the derivatization process.

A C_2 cartridge, an SCX cartridge, and an SAX cartridge were connected in series. Two cartridge combinations (C_2 + SCX + SAX) were required for each 4L sample. A reservoir was attached to the top of the C_2 cartridge and the following solvents were drawn through under pressure in succession at about 10 mL/min through each cartridge set; deionized water (100 mL), acetonitrile (30 mL), methanol/ethyl acetate/water (40:10:1, 20 mL), methanol (50 mL), acetone/dichloromethane (3:2, 50 mL), and acetonitrile (50 mL).

The C_2 cartridge was then detached from the SCX/SAX pair and water (100 mL) drawn through the C_2 leaving about 4 mL water in the cartridge above the packing. The SCX/SAX cartridges remained in acetonitrile until required for the sample elution stage.

Effluent samples contained suspended material, which was not separated prior to SPE extraction. The effluent samples were allowed to settle for several hours without movement before the extraction to avoid the solids subsequently being aspirated early on during SPE extraction, which would have caused reduction of the flow to the cartridge. Each sample was aspirated through two C_2 cartridges in parallel with a flow of about 10 mL/min. Fine suspended material, when trapped on the frit on the top of the cartridge, decreased the flow rate and it was then necessary to increase the suction. In the event of the flow decreasing to unacceptable levels for total extraction within 24 h, the tubing connector was removed and the frit pierced with a fine needle several times.

After extraction of all the sample was complete, a clean C_{18} cartridge was connected to the top of the extraction cartridge to act as an air filter. Full vacuum was then applied to the cartridges to dry them over a period of at least 16 h.

The AE were eluted from the C_2 extraction cartridge through a conditioned SCX/SAX pair with acetonitrile (fraction 1) followed by methanol/ethyl acetate/water (40:10:1 v/v) (fraction 2).

Fraction 1 was evaporated to about 10 mL and fraction 2 evaporated to complete dryness under a gentle stream of nitrogen at about 30 °C. Four fractions from each sample were then combined for derivatization. Extracts were derivatized after addition of 15 μg internal standard by adding 200 mg 2-fluoro-*N*-methyl pyridinium toluene sulfonate reagent and 100 μL triethylamine and shaking these samples for 2 h. The acetonitrile was evaporated off with a stream of nitrogen to leave a viscous yellow oil, which was dissolved in a mixture of water and acetonitrile (3:2 v/v, 1 mL) for LC/MS analysis. If the final extract was cloudy, it was filtered through a 0.2μm PTFE syringe filter.

2.5. Standard preparation: alcohol ethoxylates

Separate stock solutions of GENAPOL C100, GENAPOL T110, and LUTENSOL AO7 were prepared in acetonitrile and diluted together in the same solvent to give a 19μg/mL AE standard solution. Different volumes of this solution were dispensed into vials with 15 μg internal standard for derivatization, to give a calibration range of 0.48–61 μg/mL total AE. Additionally, the top standard was fortified with mixed alcohols prior to derivatization to increase their calibration range.

2.6. Blanks and recoveries

With each batch of samples, a blank sample (4 L) was analyzed to ensure that no significant contamination was present. Following initial analysis of the effluents from the EU monitoring survey samples were selected for recovery. A 4L sample of an effluent was fortified with a standard alcohol ethoxylate solution and linear alcohol solution. The concentration at which the sample was fortified depended on the concentration of AE found in the sample. A volume of 19 μg/mL reference solution in acetonitrile was pipetted into the sample at about 5–10 times the alcohol ethoxylate concentration (not including the free alcohol concentration) found. In addition, the effluent was fortified with the 10 μg/mL free alcohol solution at about 5–10 times the native concentration. This range was not always possible for each alcohol as the relative concentrations of the six alcohols found in the effluent did not match those in the standard.

In the case of the Canadian study, duplicate samples of four of the effluents were spiked in the field with NEODOL 25-9 at the time of sampling to check on the integrity of

the samples during storage and transit. In addition, two recovery experiments were performed on samples of deionized water (4 L) containing 8% (v/v) formalin by fortifying with either 38 μg of the reference AE mixture or with 16.7 μg of NEODOL 25-9. The fortified effluents were then processed through the extraction and derivatization stages as described previously.

2.7. Analysis of derivatized extracts

The mass spectrometer, configured for electrospray LC/MS, was set up in multiple ion monitoring mode to acquire data from relevant ions (target and internal standard) during the chromatographic run: time-windowing of the ions was required due to the large number of analyte ions. Two injections were required to monitor the whole range of different ions.

The HPLC gradient program used for all analyses started at 60/40 water/acetonitrile, was held for 5 min, and was then changed to 10/90 water/acetonitrile over the next 55 min. The mobile phase was changed to 100% acetonitrile in the next minute and held for 7 min before returning to the initial conditions. The total run time was 75 min. Aqueous and organic solvents contained 10 mmol formic acid.

Chromatograms showing typical elution profiles for the total ion response and the specific ion monitoring are presented in Figs. 1 and 2, respectively.

Calibration was carried out by constructing response factor calibration graphs where each alcohol ethoxylate target ion was measured relative to the internal deuterated standard with the same EO chain length; i.e., $C_{12}EO_4$ was calibrated against $C_{13}D_{27}EO_4$. The resultant set of calibration files were used for the quantitation of unknown samples. Typical correlation coefficients for the calibration lines for the different ethoxymers ranged from 0.90 to 0.99 (mean 0.98).

This quantitation was carried out using the software available within the MS data system. Each peak measurement was viewed manually because it was possible for the data system to select the wrong peak when a significant artifact peak was close to the analyte peak.

For sample analysis, quantitation was carried out using the calibration graphs previously obtained. The mass (ng) of each component present in each sample injection was automatically calculated from the calibration data. In the event that the peak ratio of a component fell outside the calibration range for that component then the solution was diluted with the zero standard. This maintained the same internal standard concentration and enabled the sample to be rerun without the need for adjustment of the internal standard amount. Confirmation that the correct peak in the effluent chromatogram had been selected for quantitation was achieved by injecting the extract spiked with a small volume of concentrated derivatized standard (e.g., 20 μl of the 60.8 μg standard to 180 μl extract) to confirm that the previously quantified peak increased in size.

The concentration of each component in the effluent was calculated using

$$\text{Concentration in effluent } (\mu g/L) = \text{ng injected} \times 10/V \times 1000,$$

where V is the volume extracted in liters (normally 4) which was corrected for the addition of preservative (i.e., 8% (v/v) formalin).

Recoveries were calculated from the ratio of the total mass (ng) of component found (minus the amount found in the unspiked water) to the mass (ng) added as a percentage. The amount of each component added (in ng) was calculated from a table of compositional data for a standard spiking solution (e.g., 19 μg/mL).

3. Results

3.1. Initial validation of the method

To validate that the pyridinium LC/MS method could be operated satisfactorily in the laboratory, a number of analytical checks were carried out before instigating the monitoring studies. These included recovery experiments for individual ethoxymers, analysis of blank samples to confirm LOQ for individual ethoxymers, and studies to check the repeatability of reanalysis or reinjection.

A typical limit of quantitation for each component in deionized water is shown in Table 3. Typical LOQs range from 0.2 to 9 ng/L (mean 2 ng/L).

Both replication and recovery values for the analysis of effluents can vary with the quality of the effluent under test. Different influent sources and sewage treatment processes will give rise to effluents that differ noticeably in the level of coextracted material in the chromatograph, resulting in differing amounts of interference for each component. For a typical UK effluent derived from a low industrial input source, the mean concentration of AE found from four replicate extractions was 2.21 ± 0.29 μg/L with a relative standard deviation (RSD) of 13% (Table 4). Similarly, the mean concentration of a single extract after four replicate injections was 2.32 ± 0.18 μg/L with an RSD of 8% (Table 5). Both sets of data indicate a satisfactory degree of repeatability, bearing in mind the complexity of the sample processing and data analysis steps in the analytical method.

Recovery of individual ethoxymers through the analytical procedure averaged $75\% \pm 31\%$. These were based on a mean of six sets of data based on UK effluents. Mean recovery data for C_{12}, C_{13}, C_{14}, C_{15}, C_{16}, and C_{18} were 97%, 84%, 89%, 70%, 73%, and 37%, respectively. Recovery values for C_{18} were the lowest, reflecting the higher hydrophobicity (cf. lower chain lengths C_{12}–C_{16}) and dependency on the quality (e.g., industrial composition) of the effluent being analyzed.

On the basis of the above data (i.e., low LOQs, satisfactory precision and recovery data), the method was considered satisfactory for applying to analysis of effluent samples from EU and subsequently Canadian monitoring studies.

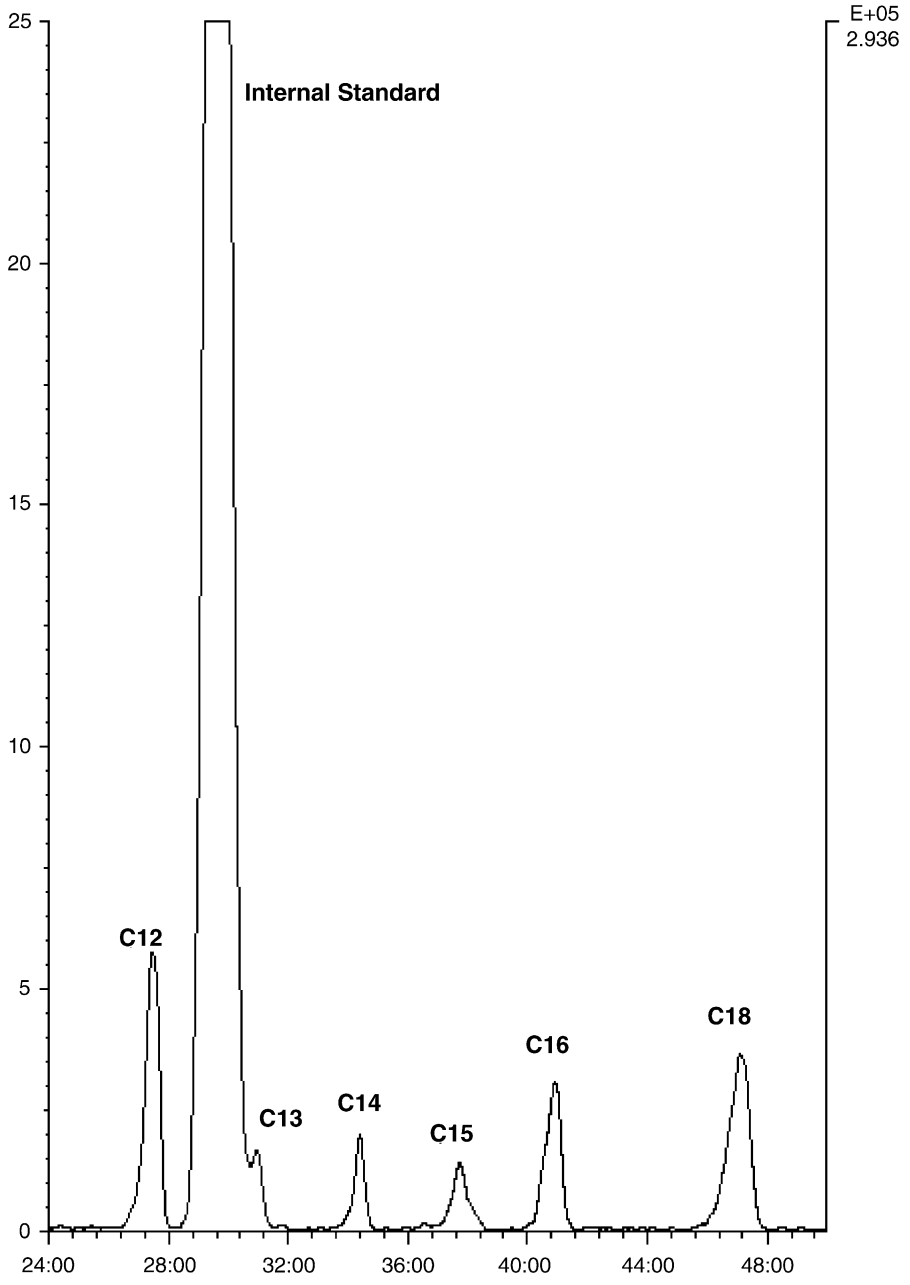

Fig. 1. Total ion current LC chromatogram showing elution of alcohol ethoxylates.

3.2. Monitoring data

Since the complete data set of 114 analytes for 20 samples is too large to include in this paper, a few examples of typical analytical results (in the form of environmental fingerprints are shown. A comparison of effluents from different sewage treatment types in Canada is shown for a rotating biological contactor (bio-film) WWTP (Table 6, Fig. 3) and an activated sludge (suspended treatment) WWTP (Table 7, Fig. 4). These data, supported by another comparison made by Morrall et al. (2005), indicate lower AE concentrations from activated sludge WWTPs. The average concentrations of AEs in activated sludge WWTP effluents ($n = 12$) from the EU monitoring survey are shown in Fig. 5. For the purposes of calculating total amounts, less than (<) LOQ figures have been treated as half their value. The environmental fingerprints confirm the extensive AE degradation across the carbon chain lengths (C_{12}–C_{18}) and the ethoxylate number (0–18).

A comparison of the levels and range of AEs and alcohols in the WWTP effluents for the EU and Canadian monitoring studies is summarized in Table 8. The analytical results are summarized for all WWTP

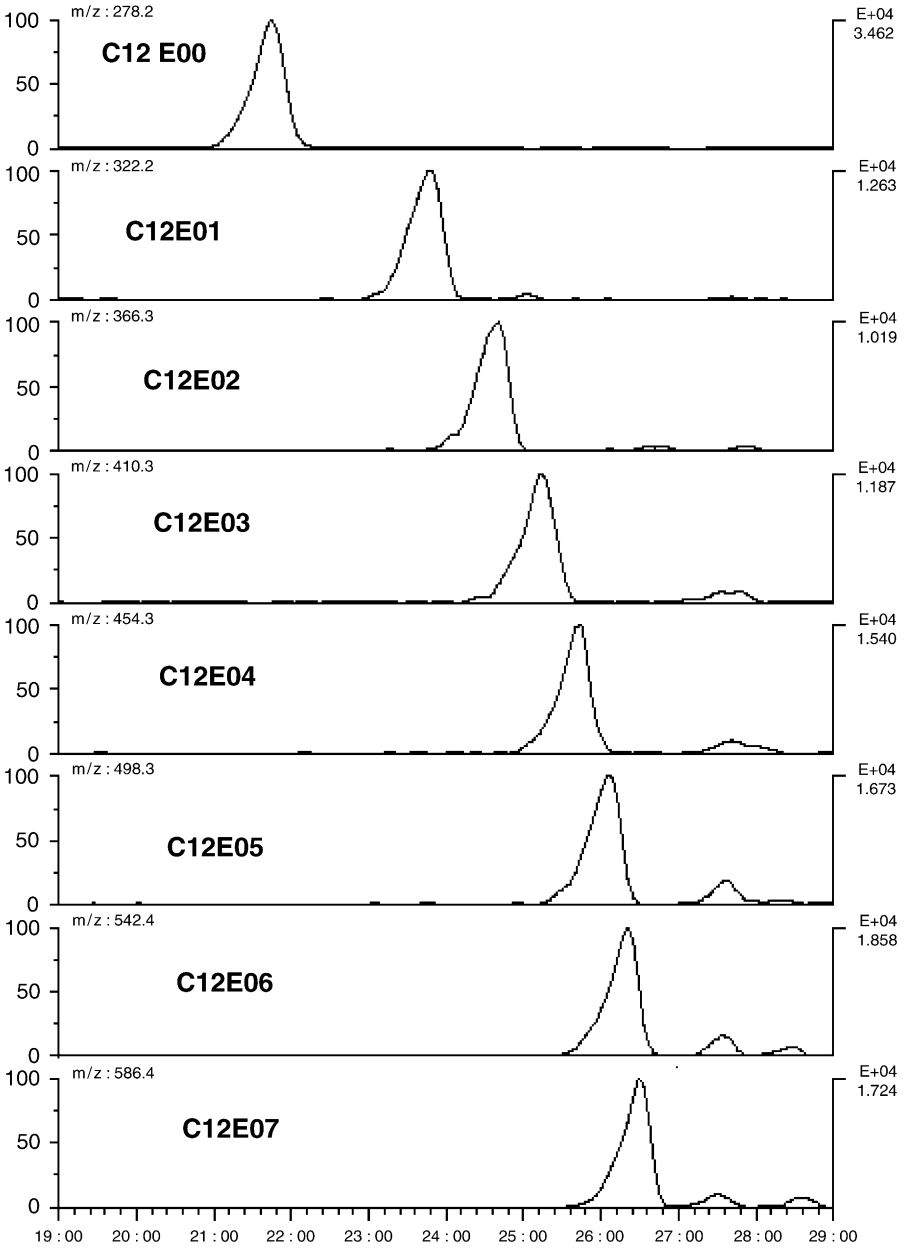

Fig. 2. Mass chromatograms showing $C_{12}EO_{0-7}$ elution.

samples collected in Europe and Canada based on either EO numbers (summed for C_{12}–C_{18} chain lengths) (Table 9) or individual carbon chain lengths (summed for EO 0–18) (Table 10). The main observation (Tables 8 and 9) is that the free alcohol (EO = 0) is the major contributor (mean 43%) to the total AE level for the WWTP effluents. One particular effluent [M (DE)] exhibited a much lower percentage of free alcohol (2%) compared with other samples. A follow-up reanalysis confirmed the low result. Overall, there is a reasonably even distribution of residues in effluents from across the C_{12}–C_{18} range (Table 10). When data are compared between EU and Canada, there are slight differences noted in discharge of C_{16} and C_{18} AE, with EU having a higher proportion (~20%) compared with Canada (~13%).

3.3. Analytical recoveries of AEs through the pyr^+ LC/MS method

Recovery analyses for the European monitoring study are summarized in Table 11 and results of the recovery and spike analyses for the Canadian samples are provided in Table 12. In the latter the values of concentration of total AE found are quoted against total concentration added. The mean recovery value for field spikes fortified with NEODOL 25-9 was 67% (range 57–75%). This is similar to

Table 3
Limit of quantitation of individual components as μg/L in deionized water (Elga Maxima Ultrapure)

EO	C_{12}	C_{13}	C_{14}	C_{15}	C_{16}	C_{18}
0	0.0010	0.0017	0.0002	0.0007	0.0002	0.0005
1	0.0012	0.0049	0.0003	0.0021	0.0002	0.0005
2	0.0009	0.0036	0.0004	0.0016	0.0011	0.0012
3	0.0010	0.0027	0.0006	0.0024	0.0005	0.0011
4	0.0005	0.0071	0.0004	0.0031	0.0006	0.0030
5	0.0013	0.0071	0.0011	0.0031	0.0010	0.0011
6	0.0008	0.0087	0.0007	0.0038	0.0006	0.0014
7	0.0012	0.0047	0.0010	0.0040	0.0008	0.0017
8	0.0014	0.0048	0.0012	0.0021	0.0010	0.0021
9	0.0017	0.0047	0.0014	0.0020	0.0011	0.0024
10	0.0018	0.0022	0.0008	0.0019	0.0024	0.0026
11	0.0019	0.0021	0.0008	0.0018	0.0031	0.0034
12	0.0018	0.0067	0.0008	0.0014	0.0026	0.0029
13	0.0017	0.0056	0.0015	0.0012	0.0025	0.0028
14	0.0015	0.0042	0.0013	0.0009	0.0023	0.0051
15	0.0013	0.0030	0.0011	0.0006	0.0040	0.0045
16	0.0021	0.0040	0.0018	0.0004	0.0033	0.0037
17	0.0046	0.0025	0.0039	0.0005	0.0028	0.0060
18	0.0023	0.0008	0.0020	0.0003	0.0018	0.0040

Table 4
Comparison of repeatability of replicate extractions of a single UK WWTP effluent

Carbon number	Total concentration (μg/L) EO_{0-18}					Standard deviation	Relative standard deviation
	Extraction No.						
	1	2	3	4	Mean	SD	RSD (%)
C_{12}	0.22	0.26	0.21	0.16	0.21	0.045	21
C_{13}	0.48	0.52	0.54	0.45	0.50	0.038	8
C_{14}	0.21	0.22	0.25	0.19	0.22	0.024	11
C_{15}	0.49	0.51	0.56	0.47	0.50	0.039	8
C_{16}	0.27	0.28	0.48	0.28	0.33	0.100	30
C_{18}	0.24	0.30	0.56	0.67	0.44	0.204	46
Total	1.92	2.09	2.59	2.22	2.21	0.286	13

Table 5
Comparison of repeatability of replicate injections of the same effluent extract

Carbon number	Total concentration (μg/L) EO_{0-18}				Standard deviation	Relative standard deviation
	Injection No					
	1	2	3	Mean	SD	RSD (%)
C_{12}	0.31	0.29	0.25	0.28	0.031	11
C_{13}	0.57	0.57	0.58	0.57	0.006	1
C_{14}	0.20	0.19	0.25	0.21	0.032	15
C_{15}	0.53	0.57	0.63	0.58	0.050	9
C_{16}	0.20	0.24	0.25	0.23	0.027	12
C_{18}	0.33	0.46	0.54	0.44	0.106	24
Total	2.14	2.32	2.50	2.32	0.180	8

the analytical recovery obtained by adding the reference C_{12}–C_{18} mix to deionized water (62%) and slightly lower than the recovery of the NEODOL 25-9 spiking solution added to deionized water (84%). These data are consistent with the previous recovery data (Table 11) from the EU monitoring study and confirm the stability of samples during transit from Canada to the UK.

Table 6
Concentration of alcohol ethoxylates in Canadian effluent C(A) from a rotating biological contactor WWTP

	Concentration (μg/L)					
	C_{12}	C_{13}	C_{14}	C_{15}	C_{16}	C_{18}
EO number						
0	1.2509	0.9607	3.3536	3.2566	3.1799	2.1743
1	0.4370	0.3223	0.0886	0.0911	0.0254	0.0161
2	0.0770	0.3701	0.0309	0.2897	0.0115	0.0075
3	0.0347	0.0299	0.0392	0.0071	0.0086	0.0093
4	0.0406	0.0214	0.0140	<0.0093	0.0107	0.0143
5	0.1263	0.1692	0.0342	<0.0092	<0.0029	0.0137
6	0.0866	0.5511	0.0374	<0.0113	0.0028	0.0329
7	0.0818	0.0691	0.0548	0.0251	0.0025	0.0140
8	0.0783	0.0338	0.0316	0.0801	0.0050	0.0317
9	0.0269	0.2668	0.1612	0.0046	0.0314	0.0120
10	0.0155	0.1744	0.4559	0.0062	<0.0071	0.0145
11	0.0385	0.1257	0.4725	0.0190	0.0110	0.0344
12	0.0664	0.0770	0.2393	0.0002	<0.0077	<0.0085
13	0.0591	0.1413	0.2061	0.0036	0.0185	0.0237
14	0.0179	0.1455	0.0857	0.0071	<0.0068	0.1038
15	0.0532	0.1319	0.0823	0.0109	<0.0120	0.0586
16	0.0090	0.0816	0.0427	0.1005	0.0182	0.1158
17	0.0284	0.1201	0.0910	0.0220	0.0223	0.2215
18	0.0087	0.2963	0.1779	0.0082	0.0054	0.1653
Total	2.5368	4.0882	5.6989	3.9469	3.3715	3.0679
Overall total	22.7102					

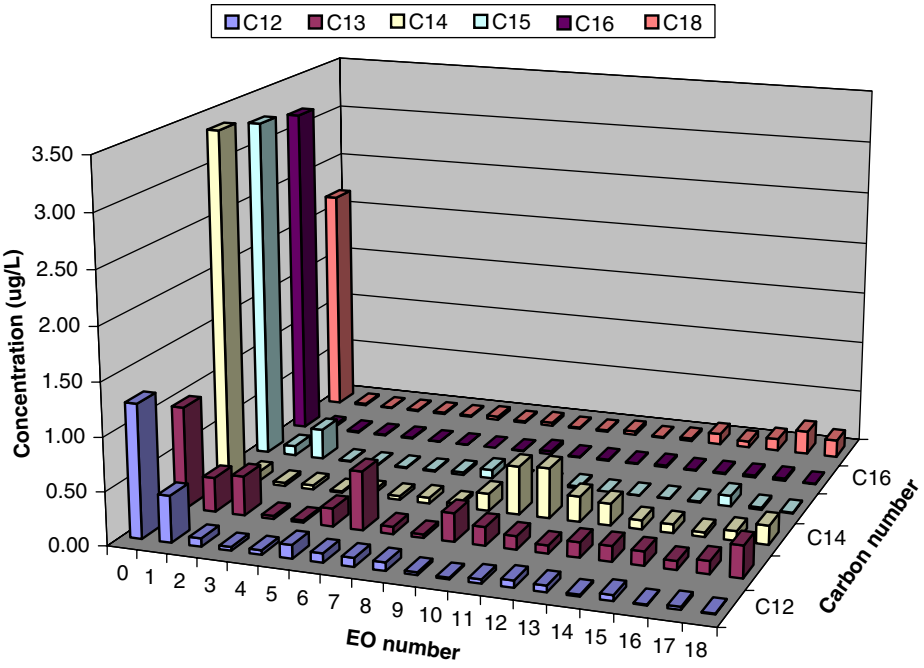

Fig. 3. Concentration of alcohol ethoxylates found in Canadian effluent C(A) from a rotating biological contactor WWTP.

Recoveries of individual ethoxymers in Table 11 average 79%. These are based on a mean of five data sets, except in a few instances where the spiking concentration was well below the natural concentration or there was chromatographic interference. Mean recovery rates for C_{12}, C_{13}, C_{14}, C_{15}, and C_{16} are 89%, 89%, 91%, 76%, and 72%, respectively. Recovery values for C_{18} are slightly lower (i.e., 55%):

Table 7
Concentration of alcohol ethoxylates in Canadian effluent W(O) from an activated sludge WWTP

	Concentration (μg/L)					
	C_{12}	C_{13}	C_{14}	C_{15}	C_{16}	C_{18}
EO number						
0	0.3007	0.1221	0.1558	0.1721	0.1602	0.1266
1	0.0699	0.0460	0.0292	0.0174	0.0038	<0.0014
2	0.0366	0.0319	0.0298	0.0045	<0.0033	<0.0036
3	0.0313	0.0140	0.0288	0.0011	0.0031	0.0048
4	0.0074	0.0071	0.0124	0.0054	0.0057	<0.0088
5	0.0338	0.0133	0.0180	0.0039	<0.0028	0.0046
6	0.0113	0.0288	0.0184	0.0032	0.0045	<0.0041
7	0.0107	0.0046	0.0239	0.0136	0.0038	<0.0051
8	0.0101	0.0090	0.0026	0.0166	<0.0029	<0.0063
9	<0.0049	<0.0138	0.0022	0.0111	<0.0033	0.1266
10	<0.0052	0.0065	0.0025	0.0130	0.0108	<0.0014
11	<0.0057	0.0116	0.0027	0.0125	<0.0090	<0.0036
12	<0.0053	Interference[a]	0.0029	0.0048	0.0128	0.0048
13	<0.0050	<0.0163	<0.0032	0.0179	0.0210	<0.0088
14	0.0052	<0.0124	0.0034	0.0371	0.0100	0.0046
15	<0.0038	<0.0088	0.0037	0.0119	0.0451	<0.0041
16	<0.0063	<0.0116	0.0039	0.0069	<0.0099	<0.0051
17	<0.0143	<0.0075	<0.0042	<0.0014	<0.0082	<0.0063
18	<0.0069	0.0035	<0.0044	0.0029	<0.0053	0.0124
Total	0.5457	0.3337	0.3461	0.3566	0.3032	0.3137
Overall total	2.1990					

[a]Gross interference in the region of the C_{13} EO_{12} peak was observed. A concentration of 0 has been used for this ethoxymer when calculating the overall total AE concentration.

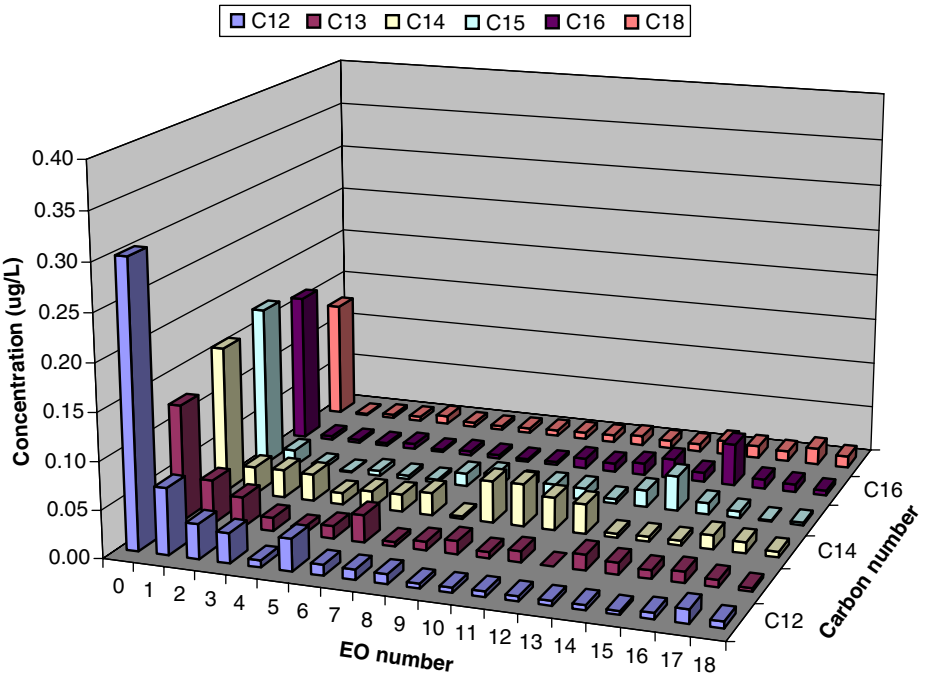

Fig. 4. Concentration of alcohol ethoxylates found in Canadian effluent W(O) from an activated sludge WWTP.

this may reflect the higher hydrophobicity (cf. lower chain lengths C_{12}–C_{16}) and dependency on the quality (e.g., industrial composition) of the effluent being analyzed. Occasional outliers did occur, possibly due to interference, but the overall pattern was reasonably consistent.

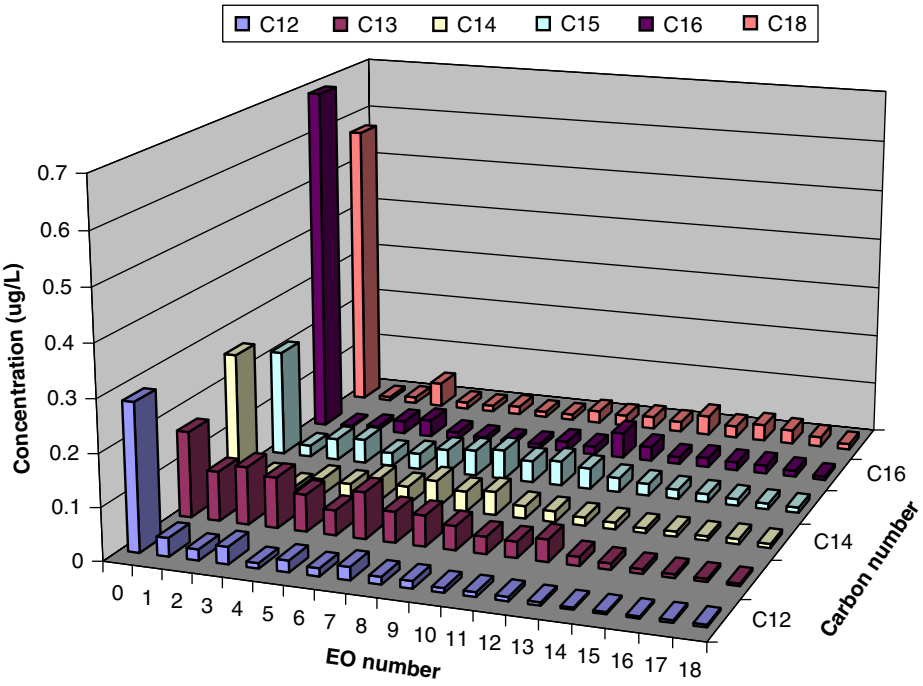

Fig. 5. Average concentration of alcohol ethoxylates in European effluents from activated sludge WWTPs.

Table 8
Comparison of AE and alcohol levels in WWTP effluents from Europe and Canada

Region	Code	Type	Total AE	Alcohol	
			(μg/L)	(μg/L)	(%)
Europe	DM (NL)	AS	8.06	1.53	19
	H (NL)	AS	5.42	2.73	50
	KV (NL)	AS	5.11	1.33	26
	N (UK)	AS	5.41	2.32	43
	C (UK)	AS	1.62	0.84	52
	R (UK)	AS	2.81	1.20	43
	E (ES)	AS	4.37	2.76	63
	V (ES)	AS	16.80	11.23	67
	M (DE)	AS	3.64	0.09	2[a]
	Ra (DE)	AS	1.08	0.32	31
	T (IT)	AS	1.82	0.74	41
	Rb (IT)	AS	2.45	0.95	40
EU range ($n = 12$)			1.08–16.80		2–67
EU mean ($n = 12$)			4.88	2.17	44
Canada	K (BC)	AS	2.72	0.85	31
	H (O)	AS	10.02	2.50	25
	LP (Q)	AS	0.96	0.30	31
	V (Q)	AS	1.21	0.29	23
	P (O)	AS	1.44	0.30	21
	W (O)	AS	2.20	1.04	47
	V (BC)	TF	13.15	3.05	23
	C (A)	RBC	22.71	14.18	62
Canada range ($n = 8$)			0.96–22.71		21–62
Canada mean ($n = 8$)			6.80	2.81	41
Overall range ($n = 20$)			0.96–22.71		2–67
Overall mean ($n = 20$)			5.65[b]	2.43	43[b]

[a]This value has been confirmed by reanalysis of the samples.
[b]The overall range and mean of all the AS effluent data are 0.96–16.80 μg/L and 4.28 μg/L. The alcohol contribution to AE levels in AS effluents is 41%.

Table 9
Summary of all the effluent results from EU and Canadian WWTPs based on EO number for C_{12}–C_{18} chain lengths

EO No.	AE levels (μg/L)																			
	The Netherlands				UK		Spain		Germany		Italy		Canada							
C_{12}–C_{18}	DM	H	KV	C	R	N	E	V	M	Ra	T	Rb	V (BC)	K (BC)	H (O)	LP (Q)	V (Q)	P (O)	C (A)	W (O)
EO0	1.53	2.73	1.33	0.84	1.20	2.32	2.76	11.23	0.09	0.32	0.74	0.95	3.05	0.85	2.50	0.30	0.29	0.30	14.18	1.04
EO1	0.34	0.28	0.19	0.05	0.13	0.27	0.07	0.50	0.08	0.07	0.07	0.17	0.54	0.05	0.24	0.02	0.02	0.02	0.98	0.17
EO2	0.32	0.26	0.20	0.04	0.08	0.16	0.08	0.49	0.16	0.11	0.24	0.26	0.49	0.06	0.24	0.02	0.02	0.02	0.79	0.11
EO3	0.56	0.35	0.40	0.04	0.07	0.21	0.11	0.41	0.98	0.10	0.04	0.11	0.26	0.02	0.08	0.02	0.02	0.01	0.13	0.08
EO4	0.48	0.24	0.38	0.04	0.05	0.10	0.06	0.14	0.47	0.04	0.03	0.10	0.22	0.03	0.04	0.02	0.02	0.03	0.11	0.04
EO5	0.50	0.20	0.33	0.04	0.05	0.11	0.05	0.19	0.28	0.04	0.05	0.18	0.49	0.03	0.20	0.02	0.02	0.08	0.35	0.07
EO6	0.80	0.19	0.51	0.05	0.09	0.09	0.07	0.22	0.21	0.04	0.09	0.16	0.75	0.05	0.26	0.04	0.03	0.11	0.71	0.07
EO7	0.80	0.18	0.34	0.05	0.14	0.18	0.04	0.20	0.20	0.08	0.09	0.17	0.56	0.04	0.40	0.05	0.04	0.13	0.25	0.06
EO8	0.65	0.14	0.23	0.05	0.20	0.30	0.03	0.14	0.24	0.07	0.12	0.12	0.82	0.13	0.40	0.10	0.02	0.13	0.26	0.04
EO9	0.40	0.20	0.23	0.07	0.16	0.30	0.14	0.41	0.25	0.04	0.05	0.04	0.47	0.04	0.24	0.04	0.10	0.03	0.50	0.15
EO10	0.35	0.14	0.20	0.06	0.13	0.22	0.15	0.28	0.17	0.03	0.05	0.03	0.64	0.05	0.35	0.03	0.07	0.04	0.67	0.04
EO11	0.38	0.10	0.26	0.06	0.10	0.31	0.16	0.45	0.15	0.04	0.05	0.04	0.72	0.08	0.53	0.04	0.09	0.03	0.70	0.04
EO12	0.29	0.11	0.17	0.05	0.10	0.25	0.18	0.37	0.11	0.03	0.03	0.03	0.80	0.10	0.48	0.04	0.11	0.03	0.39	0.03
EO13	0.28	0.07	0.08	0.04	0.07	0.14	0.09	0.26	0.08	0.03	0.03	0.03	0.85	0.15	0.60	0.04	0.12	0.03	0.45	0.05
EO14	0.25	0.08	0.07	0.03	0.05	0.16	0.15	0.22	0.05	0.02	0.02	0.01	0.59	0.16	0.51	0.03	0.09	0.05	0.36	0.07
EO15	0.12	0.06	0.06	0.03	0.03	0.12	0.09	0.40	0.05	0.01	0.02	0.01	0.48	0.16	0.52	0.02	0.04	0.08	0.34	0.07
EO16	0.10	0.04	0.06	0.03	0.05	0.07	0.06	0.40	0.04	0.01	0.04	0.01	0.40	0.16	0.81	0.05	0.03	0.09	0.37	0.03
EO17	0.07	0.04	0.04	0.03	0.04	0.06	0.05	0.31	0.04	0.02	0.05	0.01	0.60	0.37	0.86	0.04	0.06	0.11	0.51	0.02
EO18	0.05	0.02	0.03	0.02	0.03	0.05	0.03	0.21	0.01	0.01	0.04	0.01	0.40	0.19	0.72	0.03	0.03	0.12	0.66	0.03
Total	8.07	5.43	5.11	1.62	2.80	5.42	4.37	16.80	3.64	1.11	1.85	2.44	13.13	2.72	10.02	0.95	1.20	1.44	22.71	2.21

4. Discussion

The range and mean of AE results for the two different sampling surveys were very similar with an overall mean AE level of 5.7 μg/L and range 1.0–22.7 μg/L (Table 8). In a similar exercise in the US using the same analytical methodology, Morrall et al. (2005) have shown AE levels in effluents ranging from 1.17 to 20.7 μg/L (mean 7.2 μg/L). In the current study it was noticeable that the major contribution to these AE values was the free alcohol content, which contributed, on average, 43% of the total AE content. This level is approximately twice as high as the contribution (18%) from alcohols to the AE level in effluents from a laboratory model continuous-flow activated sludge (CAS) plant fed AE and operated under laboratory-controlled conditions (Wind et al., 2005). Comparison of the two studies, one a laboratory-controlled study aimed specifically at examining the fate of a known AE mixture and the second a field study examining the AE levels in effluents from WWTPs that receive a complex range of surfactants and alcohol precursors, suggests that the higher percentage of alcohols (43%) in the current monitoring study arises as a result of alcohols derived from other (non-AE) sources.

A better understanding of the sources of fatty alcohols in influents and effluents is now required. Fatty alcohols are used in a number of consumer products and pharmaceutical applications, are components of anionic (alcohol sulfates and alcohol ethoxysulfates) and non-ionic surfactants (AEs), and are formed from the microbial degradation of these surfactants (A.D. Little, 1977). They are also natural components of wastewater influent and effluent from normal biological processes and can be produced by degradation of vegetable and animal matter (Leeming et al., 1994). Typically, the fatty alcohol composition of commercial AEs are low (typically ~1–2%; Shell internal data).

A recent study of the fate of AE homologues (Wind et al., 2005) has confirmed that the most significant fraction of AE was associated with sludge, leading to low effluent concentrations. The authors confirmed that in a CAS effluent containing a low level (6–7 mg/L) of suspended solids >80% of the total AE was associated with the dissolved phase. During the sample extraction stage for effluents, it is anticipated that any AE adsorbed to solids will be trapped on the SPE cartridge and desorbed from solids by solvent. The final solvent extract, which is subsequently derivatized and analyzed by LC/MS, should therefore reflect the total AE content (both dissolved in the aqueous phase and adsorbed to particulate matter) of the effluent sample. To reflect only the bioavailable portion of AE in effluents, Van Compernolle et al., (2005) have developed a model based on sorption studies of pure AE homologues of known chain length and ethoxylation that can be reapplied to estimate the bioavailability of environmental fingerprints of AE mixtures.

Table 10
Summary of effluent results from EU and Canadian WWTPs based on individual alkyl carbon chain lengths

Sample	AE levels (μg/L)						
	C_{12}	C_{13}	C_{14}	C_{15}	C_{16}	C_{18}	Total
Netherlands							
DM	0.70	2.29	1.55	1.97	1.04	0.50	8.07
H	0.69	1.13	0.65	0.68	0.87	1.41	5.43
KV	0.84	1.78	0.77	0.76	0.62	0.33	5.11
UK							
C	0.15	0.25	0.20	0.44	0.22	0.36	1.62
R	0.25	0.34	0.44	0.92	0.41	0.45	2.81
N	0.65	1.06	0.85	1.22	0.87	0.76	5.42
Spain							
E	0.30	0.51	0.34	0.53	1.22	1.48	4.37
V	1.54	2.30	2.12	1.46	5.28	4.09	16.80
Germany							
M	0.34	1.00	0.83	0.49	0.45	0.54	3.64
Ra	0.13	0.26	0.15	0.19	0.12	0.24	1.11
Italy							
T	0.30	0.59	0.11	0.19	0.50	0.13	1.85
Rb	0.36	0.46	0.16	0.43	0.27	0.77	2.44
Canada							
V (BC)	4.47	1.80	2.55	1.74	1.23	1.34	13.13
K (BC)	0.54	0.45	0.37	0.63	0.29	0.46	2.72
H (O)	0.94	1.86	2.40	1.94	1.98	0.90	10.02
LP (Q)	0.18	0.22	0.13	0.17	0.12	0.14	0.95
V (Q)	0.15	0.19	0.21	0.38	0.09	0.18	1.20
P (O)	0.19	0.18	0.13	0.39	0.21	0.34	1.44
C (A)	2.54	4.09	5.70	3.95	3.37	3.07	22.71
W (O)	0.55	0.33	0.35	0.36	0.30	0.31	2.21
Overall mean	0.79	1.05	1.00	0.94	0.96	0.89	5.65
% of total	14	19	18	17	17	16	
Canada	1.20	1.14	1.48	1.20	0.95	0.84	6.80
% of total	18	17	22	18	14	12	
Europe	0.52	1.00	0.68	0.77	0.99	0.92	4.89
% of total	11	20	14	16	20	19	

The analytical method can be used to measure concentrations of each of the 114 different homologues (based on chain lengths C_{12}–C_{16}, plus C_{18} and ethoxymer numbers from 0–18) present in effluent samples. The homologue-specific distributions (or environmental fingerprints) from these and other US effluents (Morrall et al., 2005) can be modified by incorporating only that alcohol derived from AE sources (the so-called "alcohol cap"; Wind et al., 2005) and by taking into account any sorption to organic carbon and suspended solids (Van Compernolle et al., 2005) on an ethoxymer-specific basis. The toxicity of individual ethoxymers to aquatic organisms is dependent on chain length and EO number. Recently, a range of new ecotoxicological data (e.g., algal, daphnia, and fish QSARs, mesocosm studies), as summarized by Belanger et al. (2005), have been generated to expand the database. The authors then integrated the exposure data and the most recent effects data in a TU-based model with effects being described as homologue-specific species sensitivity distributions. Acquisition of the detailed environmental concentrations of AEs (i.e., environmental fingerprints) is therefore critical to enable robust risk assessments from the European, Canadian, and US studies, which conclude low levels of risk for AEs in the aquatic environment for these countries (Belanger et al., 2005).

To confirm the consistently high contributions from alcohols to the total AE levels in effluent samples, an alternative analytical method using different derivatization and analytical determination steps was used (Sherren, 2003). The method was based on extraction using C8 SPE cartridges, two-stage elution of alcohols,

Table 11
Recovery (%) of alcohol ethoxylates added to EU effluents

EO No	C_{12}	C_{13}	C_{14}	C_{15}	C_{16}	C_{18}
0	74	97	72	52	54	19
1	104	75	112	79	47	56
2	98	71	146	87	49	26
3	105	80	88	38	42	23
4	74	91	89	62	61	27
5	89	83	99	67	71	30
6	88	84	73	63	65	34
7	90	94	64	52	57	38
8	91	97	74	53	60	39
9	76	79	81	81	70	57
10	77	82	90	87	76	64
11	76	78	80	79	73	59
12	88	78	85	89	82	68
13	87	89	86	81	82	91
14	88	86	93	82	87	73
15	88	90	89	70	85	71
16	97	106	107	107	95	76
17	90	110	98	105	104	88
18	116	105	106	160	99	98
Mean	89	89	91	76	72	55

Table 12
Recovery (%) of alcohol ethoxylates added to Canadian WWTP effluents as field spikes or to deionized water at the time of extraction

	Recovery (%) of alcohol ethoxylates when spiked to effluent samples or water "blanks"					
	Water (a)	Water (b)	Code W(O)	Code V(Q)	Code LP(Q)	Code H(O)
Spiked (μg/L)	9.10[a]	4.18	20.67	20.67	20.67	20.67
Found (μg/L)	5.60	3.49	14.77	13.20	11.86	15.43
Recovery	62	84	71	64	57	75

[a]Water (a) was spiked with C_{12-18} AE mixture, whereas water (b) and all four effluents were spiked with NEODOL 25-9.

derivatization using a silylating reagent (MSTFA), and GC/MS analysis using single ion monitoring of the respective alcohols. A limited comparison of alcohols in effluents using the two methods gave confidence that the high level of alcohols found in the current study were correct. It also confirmed that low levels of fatty alcohols are present in many reagents and laboratory media and stresses the importance of checking for their presence in solvents before using them. Moreover, glassware should be thoroughly cleaned and rinsed with deionized water and solvents, and any possible contact from hands or gloved hands with equipment that could ultimately be contacted with solvent and reach the final extract should be avoided. Such precautions are essential for ultra-trace analytical work, which involves detection of 114 individual alcohol ethoxylate species at the ng/L level.

The estimation of the recovery of an analyte is a well-established and essential part of validating an analytical method, especially important in ultra-trace analysis of substances in complex matrices. However, the use of recovery information to "correct" analytical results—i.e., provide an estimate of the true concentration of the analyte—is a contentious issue, seen either as a natural extension of the analytical method or as an illegitimate adjustment of the results. IUPAC (1999) has provided some guidelines on the issue, which include the following arguments against correction.

- Estimated recoveries based on spiking and allied methods may be higher than the true recovery of the native analyte. Corrected analyte concentrations would still have a negative bias.
- Estimated recovery factors may be suspect because recovery may vary among matrices and according to the concentration of the analyte and interfering substances.
- Small deviations from unity in recovery estimates could result from random errors rather than from systematic loss of analyte (this accounts for recovery estimates greater than unity, which are often encountered). In this situation, applying a correction would

inflate the absolute uncertainty of the corrected result.
- Estimates of recovery often have a high relative uncertainty. This sometimes causes a recovery-corrected result to have a much higher relative uncertainty than an uncorrected result. The high uncertainty may, in turn, undermine the credibility of the analysis.
- Some legislation imposing maximum limits on contaminants is framed on the understanding that uncorrected results will be used for enforcement purposes.

The IUPAC guidelines advise that the decision whether to correct for recovery must depend on the circumstances. In the case of analysis of AE from effluents, the analyte is not a discrete defined chemical entity but rather a complex mixture of 114 ethoxymers of varying physicochemical properties. This complex mixture is extracted from environmental matrices (i.e., effluent), which contain competing coextractives that vary in concentration from sample to sample, resulting in different recoveries for each ethoxymer and for each sample. Furthermore, the recoveries from effluent samples are a function of the relative proportions of the AEs in the soluble and solid fractions and this is dependent on the suspended solids content of each sample. To address these concerns one would need to perform recovery determination on every sample; however, this is not a practical nor an economically viable proposition for analyses using the pyr+ LC/MS method.

The analytical recovery efficiencies for AEs in effluent samples were measured by spiking effluent samples with a standard solution of AEs since only a limited range of the pure individual ethoxymers are available commercially. Consequently, the degree of uncertainty of recovery for the low- and high-EO number components was expected to be high because of the low spike concentration of these species relative to background and due to the limited precision of the analysis at these low levels.

The combination of the factors given above led to the conclusion that estimates of recoveries for individual ethoxymers, and thus total AEs, could have a high degree of uncertainty, which if used to adjust the analytical data could cause the recovery-corrected results to have a much higher relative uncertainty than the uncorrected results. Hence it was considered to be inappropriate to adjust the sample pyr+ LC/MS analytical data reported here for individual ethoxymer or total AE recoveries.

5. Conclusions

A selective and sensitive analytical method for the determination of AE in effluents, which enables the full range of AE components to be determined at ng/L levels in the same analysis, has been used in municipal WWTP monitoring surveys. Such surveys in Europe and Canada employing the new methodology have confirmed low levels of AEs ($<5\,\mu g/L$) in effluents, which are in line with other monitoring studies, where removals have been high (e.g., $>98\%$). It was noticeable that the major contribution to these AE values was the fatty alcohol content. As alcohol and other low EOs are the components with the highest toxicity (cf. higher ethoxymers), aquatic risk assessments of AEs must in the future be based on monitoring studies that employ this state of the art analytical methodology. Comparison of the monitoring data with effluent data from a laboratory model of a continuous-flow activated sludge plant fed AE in an OECD synthetic sewage and operated under laboratory-controlled conditions (Wind et al., 2005) suggests that the higher percentage of alcohols in the current monitoring study arises as a result of alcohols derived from other (non-AE) sources.

Further work is needed to elucidate the composition and origins of the alcohol fraction reported and this needs to be considered if data are to be used in an aquatic risk assessment of linear AE.

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